Ultrasonically-induced degradation of microcystin LR and RR
Identification of byproducts and effect of environmental factors

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Introduction

Microcystins (MCs) are a family of strongly hepatotoxic peptides produced by different species of cyanobacteria commonly found in lakes, water reservoirs, and recreational facilities. The increased eutrophication of fresh water supplies has led to the increase in the incidence of cyanobacteria blooms and concerns over the public health implications of these toxins in the water supply. Conventional water treatment methods are poor at removing low concentrations of the cyanotoxins, and specialized treatment is usually necessary for treatment of contaminated water.

Hypotheses

Advanced oxidation technologies (AOTs) employ photochemical and radical processes for the oxidation of pollutants. While AOTs have shown tremendous promise for the remediation a variety of anthropogenic pollutants, there has been a limited number of reports on the remediation of naturally occur toxins by AOTs. Unlike AOTs involving photochemical process, ultrasonic irradiation can be used for slurries and turbid solutions such as those encountered during cyanobacterial blooms. Ultrasonic treatment is a reagent-free process and does not produce disinfection by-products. We hypothesize that ultrasonic irradiation can be used to effectively destroy MCs.

Methods

Purification of MC-LR from a laboratory culture, the ultrasonic irradiation, HPLC, and LC-MS procedures are available from the literature. Microcystin-RR was purchased from ALEXIS.

Results

Ultrasonic irradiation leads to the rapid degradation of MC-LR and dramatically reduces the PP1 toxicity of the treated solution. Hydroxyl radical is responsible for a significant fraction of the observed degradation, but other processes (hydrolysis/pyrolysis) are also important. The decomposition products of the ultrasonic destruction of microcystin-LR and microcystin-RR were analyzed by liquid chromatography-mass spectrometry (LC-MS) and the mechanisms of degradation involve oxidation of the Adda moiety. The effects of pH, Fe^{2+} and H_2O_2 on the ultrasonic degradation were investigated.

Conclusions

The major by-products of ultrasonically induced degradation of MCs result from hydroxyl radical attack on the benzene ring of Adda, substitution and cleavage the Adda conjugated diene structure. The initial rate of MC degradation is strongly pH dependent, in a manner mirrored by the pH dependence of toxin hydrophobicity. While hydroperoxide and organic peroxides are formed during ultrasonically induced irradiation of MCs, addition of Fe^{2+} effectively destroys the peroxides and promotes further oxidation of the MCs. These findings suggest that ultrasonically induced irradiation may be a suitable method for the treatment and detoxification of MCs in drinking water and in response to bioterrorism.